INFLUENCE OF DIFFERENT CATALYSTS ON TRANSESTERIFICATION OF SUNFLOWER OIL

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ABSTRACT

Biodiesel, nontoxic environmentally-friendly renewable fuel, is a mixture of different fatty acid methyl esters produced by transesterification of vegetable oil triglycerides. Content of particular FAMEs is one of the qualities of biodiesel that is regulated (standard EN 14214). FAME composition of biodiesel depends upon the feedstock and its quality. In Serbia for production of biodiesel rapeseed and sunflower oil (SFO) are mostly used, although waste frying oil from household and restaurants is possible and economically more favorable feedstock.
Since transesterification of triglycerides is catalyzed reaction, aim of this work was to investigate the influence of different catalysts on FAMEs yield. NaOCH3, NaOH and KOH with HCl were studied as the catalyst for reaction of transesterification. FAMEs mixtures derived by transesterification of refined and different waste frying SFO samples in the presence of mentioned catalysts were qualitatively and quantitatively analyzed using gas chromatograph coupled with mass spectrometer as a detector.
Content of FAMEs was the highest both for refined and waste frying SFOs when KOH and HCl were used as catalyst for transesterification. The method which uses KOH and HCl as catalyst was the fastest among investigated methods.

1. INTRODUCTION

A shortage of fossil fuel recourses, alongside high prices of these fuels, has caused intensive researches in the field of renewable fuels. Biodiesel is nontoxic environmentally-friendly renewable fuel which is produced from animal fats and vegetable oils. It can be used solely, or as a mixture of different ratios with fossil diesel, as a fuel for diesel engines. Biodiesel is a mixture of fatty acid methyl esters (FAMEs) that are produced by transesterification of triglycerides of vegetable oils or animal fats. In Serbia the most important feedstock for production of biodiesel are rapeseed and sunflower oil. Although vegetable oils are main feedstock for biodiesel production, waste frying oils from restaurants and households are possible and economically more favorable feedstock. Properties of biodiesel are regulated by standard EN 14214, which specifies, among others, the FAMEs content in fuel [1]. This content, on the other hand, depends upon feedstock qualities, as well as production i.e. transesterification method.
Transesterification (alcoholysis) is catalyzed reaction of vegetable oils' triglyceride and alcohol, usually primary or secondary aliphatic ones, resulting in a formation of fatty acid alkyl ester and glycerol. In a case of methanol, as mostly used alcohol, different fatty acid methyl esters (FAMEs) are obtained [2, 3]. Wide range of parameters has an influence on the rate of the transesterification of the triglycerides from vegetable oils: molar ratio of the reactants, temperature, reaction time, stirring rate and type of catalyst [2, 3]. Possible catalysts for transesterification are acid, alkali or enzyme. According to the literature data reaction with alkali catalysts is faster that the transesterification with acid catalysts and less

corrosive. Researches of enzymatic catalysts have started recently; however, their use is still expensive and time-consuming. Possible alkali catalysts are NaOH, KOH, $NaOCH_3$, $KOCH_3$ and carbonates [2, 3].
In this work the influence of three alkali catalysts namely NaOH, $NaOCH_3$ and KOH with HCl was investigated with aim to determine which one gives the highest yield of FAMEs. Gas chromatography coupled with mass spectrometry was used for qualitative and quantitative determination of FAMEs content in samples of transesterified refined (RSFO) and waste frying sunflower oil (WFSFO). The results of transesterification of WFSFO were compared with the results of RSFO.

2. EXPERIMENTAL

2.1. Materials

Two WFSFO samples, one collected from household and the other from restaurant, with experimentally measured iodine numbers 104.76 and 101.62 and acid values 2.21 and 2.58, respectively, and RSFO sample with an iodine number of 113.94 and an acid value of 6.68 provided by "AD Dubravka", were used for transesterification. For GC-MS analysis FAME mix C8-C22 18920-1AMP, producer Supelco, Bellefonte was used as external standard.

2.2. Methods

The Hanus method for the iodine number [4] and the AOCS Cd 3a-63 method for the acid value [5] were used in this work.
Acid value is determined by neutralizing 1-2 g of oil diluted in 50 ml of acetone with 0.1M solution of KOH in alcohol in the presence of phenolphthalein as an indicator.
Transesterification of 100 mg of oil sample with 10 ml of freshly prepared 0.28M solution of $NaOCH_3$ in methanol is done on 75°C for 20 minutes with constant stirring rate 1000 rpm in round bottom flask equipped with condenser. Mixture is transferred into the separation funnel where 20 ml saturated NaCl solution is added. FAMEs are extracted by adding 10 ml diethylether and 50 ml distillated water. FAMEs from water layer are extracted one more time with 15 ml diethylether after separation of the layers. Organic layers from first and second extraction are joined are dried by adding Na_2SO_4. Sample is left over night, filtrated and evaporated (35°C, atmospheric pressure) to 1 ml [6].
Transesterification with NaOH is used for neutral oils with acid value below 2. 0.5 ml methanol solution of NaOH (1 mol/l) is added to mixture of 4 g oil and 40 ml methanol. Mixture should be heated up to a boiling point. The reaction reaches end point when mixture becomes clear usually after 5-10 minutes. After cooling, 20 ml heptane and 40 ml water are added to the mixture. FAMEs layer is separated and dried with Na_2SO_4. After filtration solvent is removed by evaporation (50°C, 150mbar) [7].
First step of transesterification with KOH and HCl is saponification of triglycerides with KOH and the second step is esterification of the soaps in the presence of HCl into FAMEs. 120 mg of oil is placed in 10 ml tube with ground cork. After adding 2.4 ml petrol ether, a mixture is shaken for 10 s. 0.6 ml methanol solution of KOH (2 mol/l) is added to the mixture which should be shaken again for 20 s. The mixture is heated for 1 minute in water bath at 60°C. After the mixture is shaken for 20 s, 1.2 ml HCl solution in methanol (1

mol/l) is added. 4 ml petrol ether is added in tube. After shaking ester layer is removed. Petrol ether is removed by evaporation in nitrogen stream up to 1 ml [8].

The cleanup of the FAME samples before GC-MS was done on silica gel column which was prepared inside Pasteur pipette. Glass wool is placed on the bottom of the pipette. 0.3 g activated silica (heated at 120°C for 2h) and 0.3 g anhydrous Na_2SO_4 are put above the wool, respectively. The column is conditioned with 5 ml cyclohexane. After the sample is applied, FAMEs are eluted with 5 ml mixture cyclohexane:ethylacetate=2:1 v/v. Elute is collected is 25 ml round bottom flask. After adding 1 ml toluene, sample is evaporated up to 1 ml.

GC/MS system consisting of instruments Trace GC and Trace MS, Thermo Finnigan, Germany with capillary column OPTIMA 240, Machery Nagel: 60m × 0.25mm ID × 0.25 μm film thickness was used for analysis of the samples after transesterification. Working temperature of GC column was programmed as follows: initial temperature 80°C, 20°C/min to 120°C, 3°C/min to 240°C that was held for 10 min. Helium flow of 1.5 ml/min was constant. 1 μl of the sample was injected automatically by AS 2000 autosampler, Thermo Finnigan, Germany. PTV injector, which was working with split ratio 10:1, had initial temperature 60°C that was constantly risen 14.5°C/min up to 260°C. MS parameters were set to following values: interface temperature 250°C, ion source temperature 220°C, ionization energy 70eV. Full scan mode was done with ion mass range 50-500 a.m.u. For quantitative analysis of the samples by external standard method SIM technique was used.

Qualitative analysis of the FAME was done applying NIST library of mass spectra for EI.

Total relative content of FAMEs which represents mass fraction of FAMEs (C14:0-C21:1) in sample after transesterification is determined by modified standard method JUS EN 14103 [9]. Methyl ester of margaric acid is used in this method as internal standard.

Relative content of each FAME was determined by modified AOAC-IUPAC method [10]. Relative content of FAMEs was calculated after assessing of correction factors for transfering area into mass fractions.

Content of each FAME was determined by external standard method. FAME standard solutions in hexane of following concentrations 0.005 mg/ml, 0.05 mg/ml, 0.25 mg/ml, 0.5 mg/ml and 1 mg/ml were used for obtaining a calibration curve. Blank sample, standards and samples were analyzed in triplicate.

3. RESULTS AND DISCUSSION

Determined acid values of the RSFO and WFSFO from household and restaurant were 6.68, 2.21 and 2.58 (analysis were done in triplicate expressing results as mean value), respectively. Since acid values of all samples were higher than 2, transesterification with NaOH was not applicable.

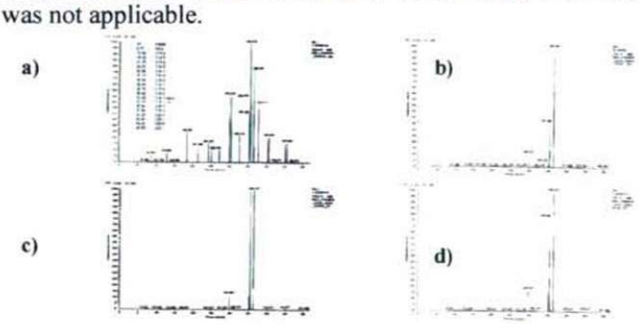

Figure 1. Chromatograms of: a) FAMEs standard and FAMEs obtained from b) RSFO c)WFSFO household d) WFSFO restaurant

Chromatograms of FAMEs standard and FAMEs obtained from RSWO, household and restaurant WFSFO when KOH with HCl was used as catalyst are shown in Figure 1. For all analyzed samples peaks of FAME C14:0, C15:0 C16:0, C16:1, C17:0 C18:0, C18:1 cis, C18:2 cis, C18:2 trans, C18:3, C16:1, C20:0, C20:1 and C20:1 are well separated.
Total relative content of FAMEs, shown in Table 1, is higher for all samples when KOH with HCl was used as catalyst, instead of $NaOCH_3$.

Table 1. Total relative content of FAMEs obtained by transesterification of RSFO and WFSFO

Sample	Total relative content of FAMEs (%)	
	$NaOCH_3$	KOH+HCl
RSFO	86.58	99.33
WFSFO Household	88.94	99.96
	79.79	96.23

Relative content of FAMEs (%) is given in Table 2. Since the standard mixture does not contain trans form of linoleic acid, content of linoleic acid was calculated as sum of its trans and cis form using correction factor for cis form. A choice of the catalyst reflected the most on the relative content of obtained FAMEs in the case of RSFO. Change of relative content of two dominant FAMEs, namely C18:1 cis and C18:2 cis+trans, for both WFSFO samples was less than 0.9%.

Table 2. Relative content of FAMEs obtained by transesterification of RSFO and WFSFO

FAME	Relative content of FAMEs (%)					
	RSFO		Household WFSFO		Restaurant WFSFO	
	$NaOCH_3$	KOH+HCl	$NaOCH_3$	KOH+HCl	$NaOCH_3$	KOH+HCl
C14:0	0.09	ND	0.07	0.05	0.14	0.11
C15:0	ND	ND	0.01	0.01	ND	ND
C16:0	5.53	6.21	7.25	6.53	9.59	9.84
C16:1	ND	ND	0.50	0.30	0.66	0.38
C17:0	ND	ND	ND	ND	ND	ND
C18:0	7.83	0.77	3.98	3.65	5.73	5.71
C18:1 cis	28.09	16.96	38.03	38.58	28.03	28.69
C18:2 cis+trans	55.92	76.07	49.19	50.17	54.86	54.44
C18:3	0.31	ND	0.15	0.10	0.18	0.10
C20:0	0.55	ND	0.18	0.13	0.22	0.19
C20:1	0.25	ND	0.18	0.13	0.22	0.18
C22:0	1.43	ND	0.46	0.34	0.37	0.35

The contents of detected FAMEs (mg/g) are given in Table 3. Total FAMEs yield was higher for all samples when transesterification was catalyzed by KOH with HCl. The highest influence of catalyst was observed when RSFO was transesterified: the FAMEs yield was 306.53 mg/g when $NaOCH_3$ was used as catalyst and 955.56 mg/g when KOH with HCl was applied as catalyst. The highest yield of FAMEs 957.32 mg/g was obtained when RSFO was transesterified in the presence of KOH with HCl.

Table 3. Content of FAMEs determined by external standard method

FAME	FAMEs content (mg/g)					
	Raw SFO		Household WFSFO		Restaurant WFSFO	
	$NaOCH_3$	KOH+HCl	$NaOCH_3$	KOH+HCl	$NaOCH_3$	KOH+HCl
C14:0	0.05	1.76	0.59	0.94	1.10	3.60
C15:0	0.08	0.29	0.17	0.13	0.12	0.23
C16:0	16.70	42.50	58.47	53.84	59.42	63.91
C16:1	1.27	3.75	4.01	4.51	4.50	5.82
C17:0	0.19	0.31	0.46	0.41	0.55	0.65
C18:0	29.02	37.09	47.59	35.82	40.24	45.02
C18:1 cis	84.75	212.53	372.06	390.86	165.01	179.42
C18:2 cis+trans	159.49	629.83	417.47	452.68	347.46	566.75
C18:3	2.52	8.26	9.23	9.64	7.81	7.94
C20:0	2.28	6.29	2.35	2.06	2.14	6.46
C20:1	2.80	3.74	1.11	1.06	0.56	0.79
C22:0	7.38	9.21	6.56	5.37	4.68	9.95
SUM	306.53	955.56	920.07	957.32	633.59	890.54

4. CONCLUSION

NaOH was not used as a catalyst since acid values of RSFO and both WFSFO were higher than 2. Total relative content of FAMEs and content of FAMEs in obtained mixture was higher for both refined and waste frying SFO when KOH with HCl was used as catalyst for trasesterification in comparison to $NaOCH_3$. Relative content of particular FAMEs is less dependent of the catalysts for WFSFOs than for the refined SFO. Transesterification of RSFO in the presence of KOH with HCl gave the highest yield.

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